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13. ABSTRACT (Maximum 200 Words) A new Nd:YAG laser was purchased using AFOSR-DURIP funds and this laser was incorporated into a new infrared laser spectroscopy system based on emerging OPO/OPA technology. This laser is now employed in the study of the IR spectroscopy of size-selected metal ion complexes. Initial results have been obtained for Mg ⁺ and Fe ⁺ ions in complexes with CO ₂ and in mixed CO ₂ /Ar complexes. The initial results are quite promising, and they suggest that this IR spectroscopy methodology will become a general way to determine the structures of clusters and to investigate their growth dynamics.					
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- Final Technical Report -

Pulsed Infrared Laser System to Study Metal Ion Solvation

AFOSR Contract No. F49620-00-1-0188

Defense University Research Instrumentation Program (DURIP)

For the Period March 31, 2000 to March 30, 2001

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OBJECTIVES

Our AFOSR research program has a goal of studying of weakly bound clusters containing metals and how their bonding interactions influence the dynamics of "solvation." Closely related to this is the desire to elucidate the interactions of light metal ions (Mg^+ , Al^+ , etc.) that are formed in meteor ablation with atmospheric gases. In this work, metal ion complexes are prepared in the gas phase via laser vaporization of solid targets. We use laser spectroscopy and mass spectrometry to measure the properties of these clusters, and comparisons are made to the predictions of theory. The work relevant for this DURIP instrumentation grant applies *infrared* laser spectroscopy for the first time to study these gas phase clusters. New kinds of IR lasers have just become commercially available, and we hope to take advantage of this new technology for improved measurements on cluster spectroscopy. This DURIP grant was for the purchase of a pump laser to be used as a component in such a new IR laser system.

STATUS OF EFFORT

Gas phase experiments on various weakly bound and strongly bound clusters are actively conducted in our labs at Georgia using two pulsed molecular beam machines equipped with time-of-flight mass spectrometers. Additional gas phase experiments are conducted on a similar molecular beam machine located at the "FELIX" free electron laser together with the group of Gerard Meijer (University of Nijmegen) at the F.O.M. Institute for Plasma Physics in Nieuwegein, The Netherlands. The infrared laser system funded from this DURIP project has been purchased and configured in the laboratory for

these molecular beam spectroscopy experiments. The laser and experiments using it are working. Preliminary presentations of the work have already been presented at meetings, and initial publications are anticipated in the near future.

ACCOMPLISHMENTS/NEW FINDINGS

Experiments on metal ion complexes investigate the details of electrostatic interactions between metal ions and small molecules. There are two areas in which such interactions are important. Meteor ablation in the thermosphere produces neutral and ionized metal atoms of sodium, magnesium, aluminum, calcium, etc., and these species condense with and/or react with atmospheric gases. Fundamental information about the energetics of electrostatic interactions and the reactivity of these metals are used in Air Force models of atmospheric chemistry. In a second area, we explore the fundamental dynamics of metal solvation. In the gas phase, small metal complexes with solvent molecules necessarily contain singly charged metal. Although the normal charge states of many metals in solution is +2 or +3, such multiply charged species spontaneously undergo charge transfer in contact with limited numbers of neutral solvent molecules in the gas phase. Larger clusters, however, are eventually able to stabilize (i.e., "solvate") multiply charged metal ions. However, the critical size required for solvation and the details of the energetics involved are not well understood.

Over the last several years, we have employed *electronic* photodissociation spectroscopy to probe the details of metal ion interactions with small molecules. Spectra have been measured recently for species such as $\text{Ca}^+ \text{-N}_2$, $\text{Mg}^+ \text{-methanol}$, $\text{Mg}^+ \text{-C}_2\text{H}_2$, $\text{Mg}^+ \text{-}$

Ne, etc. Vibrationally resolved electronic spectra were obtained and in some case the spectra were rotationally resolved. These experiments were ground breaking in that the first detailed spectroscopy was obtained for metal cation complexes with water ($\text{Mg}^+-\text{H}_2\text{O}$, $\text{Ca}^+-\text{H}_2\text{O}$) and for metal cation π -complexes (Ca^+ -acetylene). However, in some respects, these electronic spectroscopy measurements are unsatisfying. Essentially no spectra with resolved vibrational bands could be obtained for any complexes with more than one ligand. This makes it impossible to study systematic trends caused by solvation or other collective ligand dynamics. Therefore, a primary goal of this work is the study of multi-ligand complexes. Another difficulty has been the comparison of our work with theory. Theory most often calculates properties of ground electronic states, while our measurements in the past focused on excited states. Another goal therefore is the development of techniques to probe the ground state of cluster molecules. Infrared spectroscopy, made possible by new IR OPO laser sources, makes it possible for us to do this. Since predissociation and other dynamical problems are less likely here, ground state studies also make it possible to study multi-ligand complexes. Our top priority, therefore, has been the modification of our machinery for IR experiments and the initiation of these new experiments. We have been extremely pleased with our initial success in this area. New IR spectroscopy experiments have been completed that make it possible for the first time to study the ground state vibrations of metal containing cluster molecules and to measure the change in these spectra for a variety of cluster sizes.

To initiate infrared experiments, we purchased a new OPO/OPA laser system and we used this DURIP grant from AFOSR to buy the pump laser (Continuum model 8010

Nd:YAG laser) to use with this new OPO/OPA. This combined laser system was delivered and assembled in the lab in the fall of 2000. It provides infrared light with high pulse energies in the region of 2000 to 4500 cm^{-1} where vibrational fundamentals for many small molecules occur. Other instrument modifications (beam purge tube, re-configured time-of-flight mass spectrometer) were completed soon after this, and IR spectroscopy experiments began in late fall 2000.

A potential problem with IR spectroscopy on M^+-L_n complexes detected by photodissociation is that the bond energies in these complexes often exceed the energy available in one IR photon tuned to a ligand vibration. For example, a $\text{M}^+-\text{H}_2\text{O}$ complex bound by the charge-dipole interaction typically has a bond energy of about 1.0 eV (8066 cm^{-1}), while the IR excitation of the O-H stretch on the water provides only 3700 cm^{-1} of energy. This kind of situation occurs generally except for the most weakly bound ligands (e.g., H_2). Photodissociation therefore should require multiple photon absorption, which may be problematic considering the relatively low absorption efficiency in the infrared. However, with the new pulsed OPO system, the IR intensity is enough to achieve such multiple photon excitation. Photodissociation is also easier, as shown recently by Mark Johnson and coworkers at Yale, if ion complexes are made with an attached rare gas atom. The binding energy of argon, for example, is quite low, and its interaction with the complex is likely to be weak enough to avoid any perturbation of the complex structure. We have therefore studied metal cation complexes made with only ligands and those "tagged" with argon to compare the spectra. We find that argon tagging does not shift the spectra noticeably in most cases, but it does increase the fragmentation yield and

narrower linewidths are obtained.

In initial studies we have examined CO_2 as the ligand because of its weak binding to many metals and because of its strong IR absorption at the asymmetric stretch resonance near 2350 cm^{-1} . We have studied complexes of CO_2 with Fe^+ and Mg^+ , with and without argon tagging. We have preliminary data for Mg^+ bound to water in the OH stretching region. Figure 1 shows spectra we have measured for small $\text{Mg}^+(\text{CO}_2)_n$ complexes for $n=1,2,3$. The vibrations are blue shifted with respect to free CO_2 . The two IR active vibrations near the asymmetric stretch region establish that the $n=2$ complex is bent, consistent with the predictions of theory. We are extremely excited about these studies, since they provide the first data for metal complex IR spectroscopy and because we are now able to study spectra as a function of complex size.

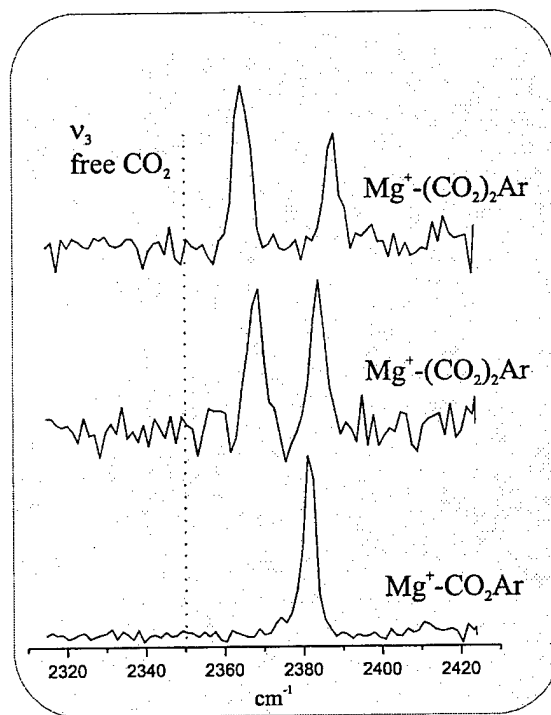


Figure 1. The IR photodissociation spectra of $\text{Mg}^+(\text{CO}_2)_n$ complexes.

PERSONNEL SUPPORTED BY AND/OR ASSOCIATED WITH THIS PROJECT

Faculty:

Professor Michael A. Duncan

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Jose Velasquez	Ph.D. program
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Areatha Knight (Ph.D. University of Georgia)
Dr. Gilles Gregoire (Ph.D. University of Paris-South)

PUBLICATIONS IN THIS FUNDING PERIOD USING THE NEW EQUIPMENT

None

INTERACTIONS/TRANSITIONS

a) PRESENTATIONS

Invited Lectures Presented by the PI on this Research

1. "Photodissociation Spectroscopy of Metal Ion Complexes," Technical University of Berlin, Germany, April 2001.
2. "Photodissociation Spectroscopy of Metal Ion Complexes," Free University of Berlin, Germany, April 2001.
3. "Infrared Photodissociation Spectroscopy of Metal Cation Complexes," Gordon Research Conference, *Photoions, Photoionization and Photodetachment*, Williams College, Williamstown, MA, July 2001.
4. "Infrared Photodissociation Spectroscopy of Metal Cation Complexes," *European Conference on Cluster Cooling*, Nieuwegein, The Netherlands, August 2001.
5. "Infrared Photodissociation Spectroscopy of Metal Cation Complexes," *Free University of Amsterdam*, Amsterdam, The Netherlands, August 2001.

Poster and Contributed Presentations of this Research

1. G. Gregoire, J. Velasquez and M.A. Duncan, "Infrared Photodissociation Spectroscopy of $\text{Fe}^+ \text{-L}_x$ Complexes", Gordon Research Conference on *Gaseous Ions: Structures, Energetics and Reactions*, Ventura, CA, February 2001.
2. G. Gregoire, J. Velasquez and M.A. Duncan, "Infrared Photodissociation Spectroscopy of $\text{Fe}^+ \text{-L}_x$ Complexes", *Air Force Office of Scientific Research Contractor's Meeting*, Newport Beach, CA, May 2001.

b) CONSULTATIVE AND ADVISORY FUNCTIONS - None

c) TRANSITIONS - None

NEW DISCOVERIES, INVENTIONS OR PATENT DISCLOSURES - None

PI HONORS/AWARDS - None